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INTERACTION OF GASES WITH LUNAR MATERIALS

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Contents

The progress report for this period consists of
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SOME SURFACE PROPERTIES OF APOLLO 17 SOILS*

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ABSTRACT

The surface chemistry of Apollo 17 lunar fines samples 74220 (the orange soil) and 74241 (the gray control soil) has been studied by measuring the adsorption of nitrogen, argon, and oxygen (all at 77°K) and also water vapor (at 20 or 22°C). In agreement with results for samples from other missions, both samples had low initial specific surface areas, consisted of nonporous particles, and were attacked by water vapor at high relative pressures to give an increased specific surface area and create a pore system which gave rise to a capillary condensation hysteresis loop in the adsorption isotherms. In contrast to previous samples, both of the Apollo 17 soils were partially hydrophobic in their initial interaction with water vapor (both samples were completely hydrophilic after the reaction with water). The results are consistent with formation at high temperatures without subsequent exposure to significant amounts of water.

INTRODUCTION

There have been, as compared to other types of experiments, relatively few studies of the surface properties of lunar soil samples. Reported results (Holmes et al., 1973b) indicate that lunar soil samples have approximately uniform surface characteristics independent of their location on the lunar surface. Major features are a relatively low specific surface area (less than one m^2/g) and non-porous particles (no pores of the type which affect gas adsorption isotherms, i.e., are less than a few hundred angstroms in size). This uniformity is not surprising if one considers that the lunar soil is produced by gardening processes such as bombardment by micrometeorites and radiation-two processes which are constant over the lunar surface. An additional common feature of lunar soil samples is their reaction with water vapor at high relative pressures. This reaction drastically alters their surface properties (Holmes et al., 1973a, 1973b; Gammage et al., 1974; Cadenhead and Stetter, 1974).

The orange and gray soils from Shorty Crater which were returned by the Apollo 17 mission provide an opportunity to check the general uniformity of surface properties of lunar soils. These two samples differ markedly in their chemical composition and petrology (LSPET, 1973). In addition, there is an order of magnitude difference in the surface exposure ages of these two samples (Eberhardt et al., 1974). If these two factors are important in determining the surface characteristics of lunar soils it should be reflected in the experimental results.

EXPERIMENTAL

The experimental measurements were made with an existing vacuum microbalance system which has been described in detail (Fuller et al., 1965). The system was equipped with a thermoelectric cooler and associated instrumentation (Fuller et al., 1972) for maintaining a constant pressure of water vapor. This is a considerable convenience and is important when working with water vapor in a glass system. Background blank corrections (these include thermomolecular flow effects, the effect of any temperature gradients, and the inherent pressure dependence of the balance zero, but do not include buoyancy corrections) and buoyancy corrections (where necessary) have been applied to all the data. The critical importance of these corrections when working with samples having small specific surface areas has been discussed (Cadenhead et al., 1972; Holmes et al., 1973a).

Experimental procedures were the same as used in our previous study (Holmes et al., 1973b). Prior to an adsorption experiment the sample was always outgassed for a minimum of 16 hr (overnight). Outgassing pressures were in the range of 10^{-5} to 10^{-6} torr (measured on a 25 mm O.D. manifold leading directly to the balance chamber). The maximum outgassing temperature used in the present study was 300°C. Measurement of the isotherms required 15 to 20 minutes for equilibrium except for water vapor at high relative pressures which required an overnight waiting period, or longer, for equilibration.

Specific lunar samples used for the present study were 74220,35 (the orange
soil from Shorty Crater) and 74241,42 (the gray control soil). Sample 74220
was unsieved while 74241 was the fine sieve fraction (< 1 mm) of the bulk
soil. A 400 mg aliquot of each sample was used without any further physical
separation. Weight determinations are estimated to be reliable to ±2 micro-
grams (±0.005 mg/g with a corresponding uncertainty in the nitrogen specific
surface area of ±0.02 m^2/g) over the extended time interval involved in
the experiments.

RESULTS

Nitrogen isotherms for adsorption on sample 74220 at 77°K are shown
in Figure 1. All of the isotherms in this paper are shown as mg of adsorb-
ate per g of sample as a function of the relative pressure P/P_o, where
P_o is the saturation vapor pressure of the adsorbate at the isotherm tem-
perature. Prior to exposure to water vapor at high relative pressures,
nitrogen adsorption on sample 74220 was reversible over the entire range
of relative pressure. Obviously this is not the case after exposure to
water as the post-water nitrogen isotherms have well defined high pressure
capillary condensation hysteresis loops. It should be emphasized that
there was no irreversible adsorption of nitrogen as all of the adsorbed
nitrogen could be removed by evacuation at the conclusion of the isotherm.

Corresponding data for the adsorption of nitrogen on the gray soil
sample 74241 are shown in Figure 2. The results shown in Figures 1 and 2
are quite similar with two exceptions. Prior to exposure to water vapor,
nitrogen adsorption on sample 74241 was independent of the outgassing

temperature. Secondly, in contrast to the results for 74220, the post-water

nitrogen isotherms for 74241 are different for the 200 and 300°C outgassings.

The isotherms shown in Figures 1 and 2 have a very common shape and fit the

general classification of Type II for the adsorption of inert gases on solid

surfaces (Brunauer, 1943).

Specific surface areas were derived from the data of Figures 1 and 2

by application of the standard BET treatment (Brunauer et al., 1938). The

resulting specific areas are given in Table I. There is good agreement

between the value for sample 74220 after outgassing at 300°C (pre-water)

and a reported value of 0.46 m^2/g (Cadenhead,1973).

Water adsorption isotherms were measured at 20°C (74220) and 22°C (74241)

after outgassing the samples at 300°C. The data below a relative pressure

of 0.5 are shown in Figures 3 and 4 for samples 74220 and 74241, respectively.

There was massive adsorption on both samples as the water vapor pressure

approached saturation but the scale used in Figures 3 and 4 is not appropri-

ate for presentation of the data. As the water vapor pressure approached

saturation maximum adsorption of water was 23.5 and 49.2 mg/g for samples

74220 and 74241, respectively. However, these are not equilibrium values

and do not, therefore, represent the maximum possible water adsorption

(sorption would probably be a better description) on these two samples.

There are some obvious differences between the adsorption and desorption

branches of both isotherms shown in Figures 3 and 4. The monolayer capacity

derived by a BET treatment (Brunauer et al., 1938) of the data for 74220

increased from 0.073 mg/g (adsorption data) to 0.466 mg/g (desorption data).

The corresponding increase for sample 74241 was from 0.050 to 0.310 mg/g.

These are more than six-fold changes as a result of one adsorption-desorption

cycle in water vapor. Desorption branches of both isotherms have evidence for a capillary condensation hysteresis loop closing at a relative pressure of about 0.35. This is in addition to the general hysteresis over the entire range of pressure. Vacuum retention of irreversibly adsorbed water amounted to 0.105 mg/g for 74220 and a massive 1.036 mg/g for 74241. A second adsorption-desorption cycle in water vapor produced little, if any, additional change in either sample although both isotherms were irreversible over the entire relative pressure range.

Oxygen adsorption isotherms for sample 74220 at 77°K are shown in Figure 5. These isotherms were measured after the reaction with water vapor. The capillary condensation hysteresis loops are more pronounced, and close at a lower relative pressure, than those obtained with nitrogen (compare Figure 5 to Figures 1 and 2). Apart from the high pressure hysteresis loops the oxygen isotherms were completely reversible. Adsorption of argon on these samples was basically very much like nitrogen and the results will not be presented.

Attempts to chemisorb carbon dioxide or oxygen on these two soil samples at room temperature were unsuccessful. These attempts were made after the reaction with water vapor and the negative results were independent of the presence or absence of chemisorbed water.

DISCUSSION

In a very general manner the results obtained with these two Apollo 17 soil samples are quite similar to reported data for samples from the Apollo 12, 14, and 16 missions (Holmes et al., 1973a, 1973b). These

similarities consist of: 1) Initially (prior to water adsorption at high relative pressures) all lunar soil samples have a low specific surface area (less than 1 m^2/g). 2) Lunar soil particles (again in the initial state) do not have a pore system of the type which affects gas adsorption isotherms (i.e., pores which give rise to capillary condensation hysteresis loops and are less than a few hundred angstroms in size) as the initial nitrogen isotherms are completely reversible over the entire pressure range. 3) Lunar soil samples are attacked by water vapor at high relative pressures. 4) The attack by water vapor increases the specific surface area and creates a pore system which gives rise to a capillary condensation hysteresis loop in the adsorption isotherms. 5) The pore system resulting from the attack by water vapor can be partially (in some cases almost completely) blocked (i.e., inert gases such as nitrogen are prevented from entering the pore system) by irreversibly adsorbed water.

In spite of the general similarity of all the results obtained to date there are significant specific differences, not only between 74220 and 74241, but also between these two and the previously studied fines (Holmes et al., 1973a, 1973b). Both of the Apollo 17 samples were partially hydrophobic in their initial interaction with water vapor (apparent water surface areas were about half of the nitrogen values). This behavior can be contrasted with the hydrophilicity of the previous samples and may be indirect evidence that the Apollo 17 samples have been heated to an elevated temperature. An example is the fact that silica, when heated to about 900 °C, becomes hydrophobic (Asher et al., 1965). However, as is obvious from Figures 3 and

4, both of the Apollo 17 samples were strongly hydrophilic after the attack by water vapor at high relative pressures.

Alteration of the two Apollo 17 samples was essentially completed with one cycle in water vapor to high relative pressures. This is sharp contrast to Apollo 12, 14, and 16 samples where the alteration process continued through several cycles (Holmes et al., 1973a, 1973b). Reasons for this difference are unknown at the present time. However, parameters such as the length of time the sample is exposed to high relative pressures of water vapor have not been quantitatively assessed.

The effect of increased outgassing temperature on the subsequent adsorption of nitrogen at 77°K (Figures 1 and 2) can be simply explained as the removal of strongly adsorbed water from narrow (less than about 20 Å) pores and pore openings. This removal allows nitrogen to enter the pores and leads to increased adsorption at all pressures and also increases high pressure hysteresis. This explanation is supported by the fact that one can reverse the effect of outgassing at, e.g., 300°C, by the simple expedient of allowing the sample to irreversibly adsorb water.

It is obvious from Figures 1 and 2 that the blocking action of irreversibly adsorbed water is very much less in the case of 74220 than with 74241. Physically there are two possible reasons for this. One is that the pore openings may be wider in the case of 74220. Secondly, there is markedly less irreversibly adsorbed water on 74220 (compare Figures 3 and 4). This latter fact may also explain the reportedly low value for "lunar" (terrestrial?) water in the orange soil (Epstein and Taylor, 1973). Both of these factors may also be related to the very high glass content of 74220 (LSPET, 1973).

The very slight dependence of the initial nitrogen adsorption on outgassing temperature (Figure 1) may also be related to the high glass content. This could be a surface "roughening" effect caused by removal of water chemisorbed in the initial exposure to the terrestrial atmosphere.

The oxygen adsorption isotherms on 74220 (Figure 5) are not unusual. Oxygen is adsorbed less strongly than nitrogen, but this is readily explained by the quadrupole moment of nitrogen. Closure of the hysteresis loop at a lower relative pressure can be attributed to the larger surface tension of liquid oxygen as compared with liquid nitrogen. The larger hysteresis loop observed with oxygen is due to two factors. One, oxygen is a smaller molecule and can, therefore, penetrate smaller pores. Two, liquid oxygen is more dense than liquid nitrogen, and thus more is required to fill a given volume. These two factors have previously been found to influence sorption results (Ridge and Molony, 1969). However, in contrast to Ridge and Molony, 1969), who used 14.1 $\overset{\circ}{A}{}^2$ for the cross-sectional area of adsorbed oxygen, we found it necessary to use 20.1 $\overset{\circ}{A}{}^2$ to make the oxygen area equal to the nitrogen value. Even though oxygen can penetrate smaller pores than nitrogen, it apparently forms a much more loosely packed monolayer.

Failure of the samples to chemisorb oxygen at room temperature can be understood in terms of the hypothesis of Cadenhead and Stetter (1974), who infer that the reduced surfaces of lunar samples are rapidly oxidized on exposure to air or oxygen. This implies that our samples were completely oxidized while they were being loaded onto the microbalance. Failure of the samples to chemisorb carbon dioxide indicates an acidic surface, which is in accord with the high silica content of the samples (LSPET, 1973).

A mechanism for the very general attack of lunar fines by adsorbed water has not been clearly established. Cadenhead and Stetter (1974) prefer a fracture process. We find it difficult to visualize how fracturing of the relatively large, micron-sized particles in lunar soils could give rise to the very small pores which can be so effectively blocked by irreversibly adsorbed water. In addition, one might expect a fracturing process to occur in the monolayer region as this is where the vast majority of the adsorption energy release occurs.

We have previously attributed the alteration of lunar samples to a leaching of material from the latent damage track by the adsorbed water film at high relative pressures (Holmes et al., 1973b). Based on the "ion explosion spike" model (Fleischer et al., 1965), this leaching process would create a system of pores having wide bodies and narrow openings. Such a pore system very nicely fits the observed characteristics of the adsorption isotherms. However, Maurette (1973) and Bibring (1974),using high voltage electron electron microscopy, were unable to detect any readily visible changes in the Apollo 16 sample 63341 that we have studied (Holmes et al., 1973b). Maurette (1973) and Bibring (1974) both conclude that the latent damage tracks have clearly not been etched. It is worth mentioning that normal track studies, using strong etching conditions, produce etched trackes in the micron sized range (e.g., Plieninger et al. 1973). The largest dimension of the pore system, as deduced from the adsorption isotherms, is at least two orders of magnitude smaller than this. Irrespective of whether the adsorbed water film is removing material from damage tracks or not, these results demonstrate the ability of gas

adsorption studies to sense physical characteristics and changes which are difficult, it not impossible, to study by other methods.

Because of the fairly wide variation in chemical composition and petrology of the lunar soil samples, one would not expect the general similarity of the results if these two factors played dominant roles in the interaction of water with lunar fines. Our previous results with the Apollo 12 samples 12001 and 12070 (Holmes et al., 1973b) clearly demonstrate that the alteration process is not a simple reaction of water vapor with an anhydrous material. Both of these samples were heated to 1000°C (in vacuum) after having reacted with water vapor. This destroyed the water induced porosity and reduced the specific surface areas to approximately their initial values. After heating to 1000°C, both samples still adsorbed large (much more than expected on the basis of physical adsorption) amounts of water at high relative pressures (above $P/P_o = 0.9$) and retained water when evacuated. The amount retained in vacuum was roughly equivalent to a chemisorbed monolayer. However, nitrogen isotherms measured before and after the reaction with water were identical. Obviously, after heating to 1000°C, the physical characteristics of the samples are not altered by the reaction with water vapor.

We are still inclined to believe that radiation damage is the dominant factor controlling the interaction of lunar fines with water vapor. However, if this is the case, it is somewhat difficult to reconcile the much younger exposure age of 74220 (Eberhardt et al., 1974) with the results of the present study. Current experiments with annealed samples should provide important information concerning the surface properties of lunar soils.

Results of the interaction of water vapor with lunar fines argue strongly against any previous exposure to significant amounts of water, whether it is volcanic, cometary, or indigenous in origin. Any model invoking such a previous exposure to water must also provide a subsequent heat treatment step to destroy the effects of such an exposure. From our previous results (Holmes et al., 1973b) a temperature in excess of 700 to 800°C would be required.

ACKNOWLEDGEMENTS

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Table I

Specific Surface Areas in M^2/g

Outgassing Temp. (°C)	Sample 74220,35	Sample 74241,42
25 (pre-H_2O)	0.35	0.36
300 "	0.42	0.37
25 (post-H_2O)	0.90	0.57
100 "	1.02	0.64
200 "	1.40	0.88
300 "	1.38	1.01

LIST OF FIGURES

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Fig. 1. Adsorption of N_2 on 74220,35 at 77 °K
Sample Outgassed at Indicated Temperature.
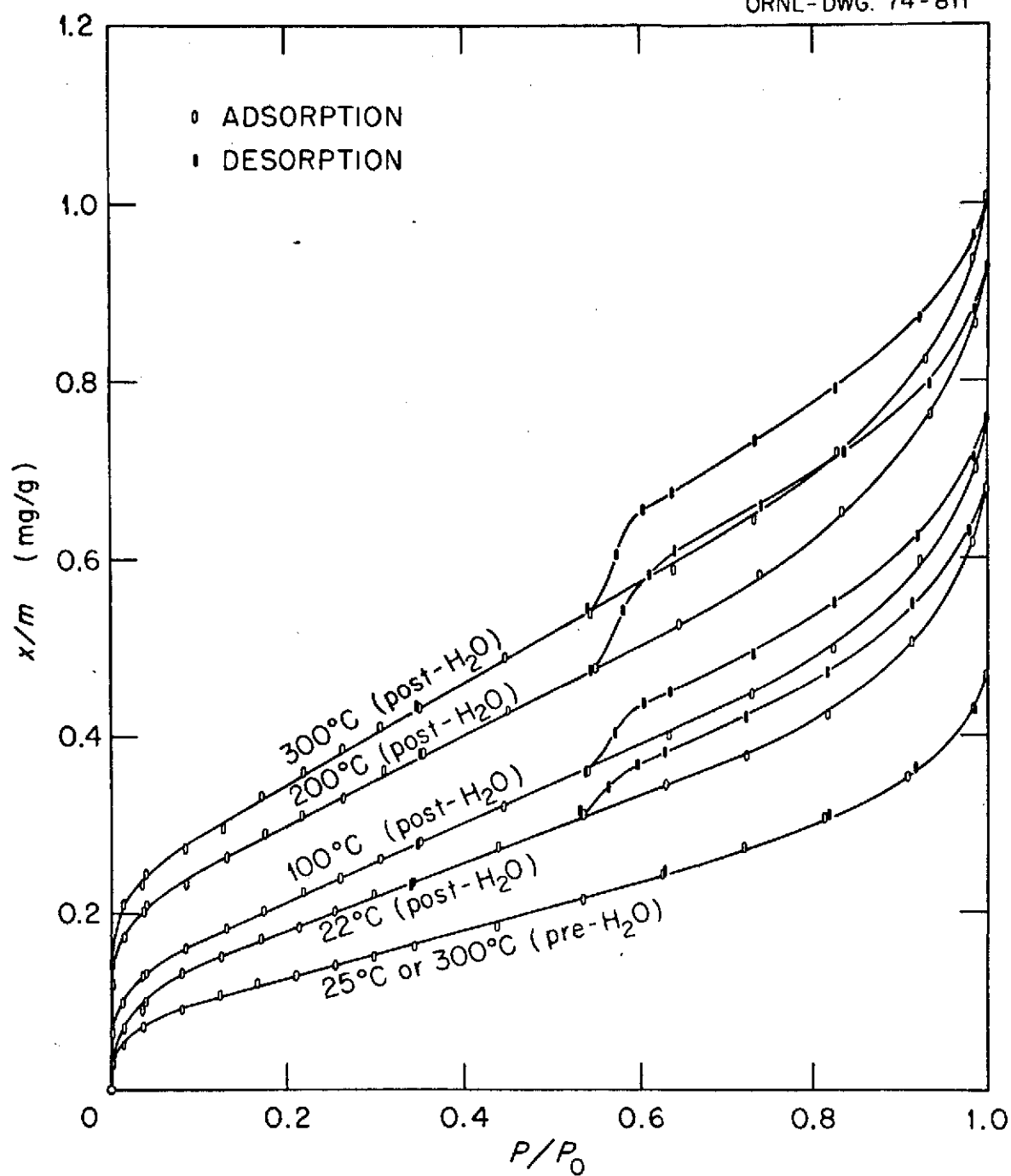
Fig. 2. Adsorption of N_2 on 74241,42 at 77°K. Sample Outgassed at Indicated Temperature.
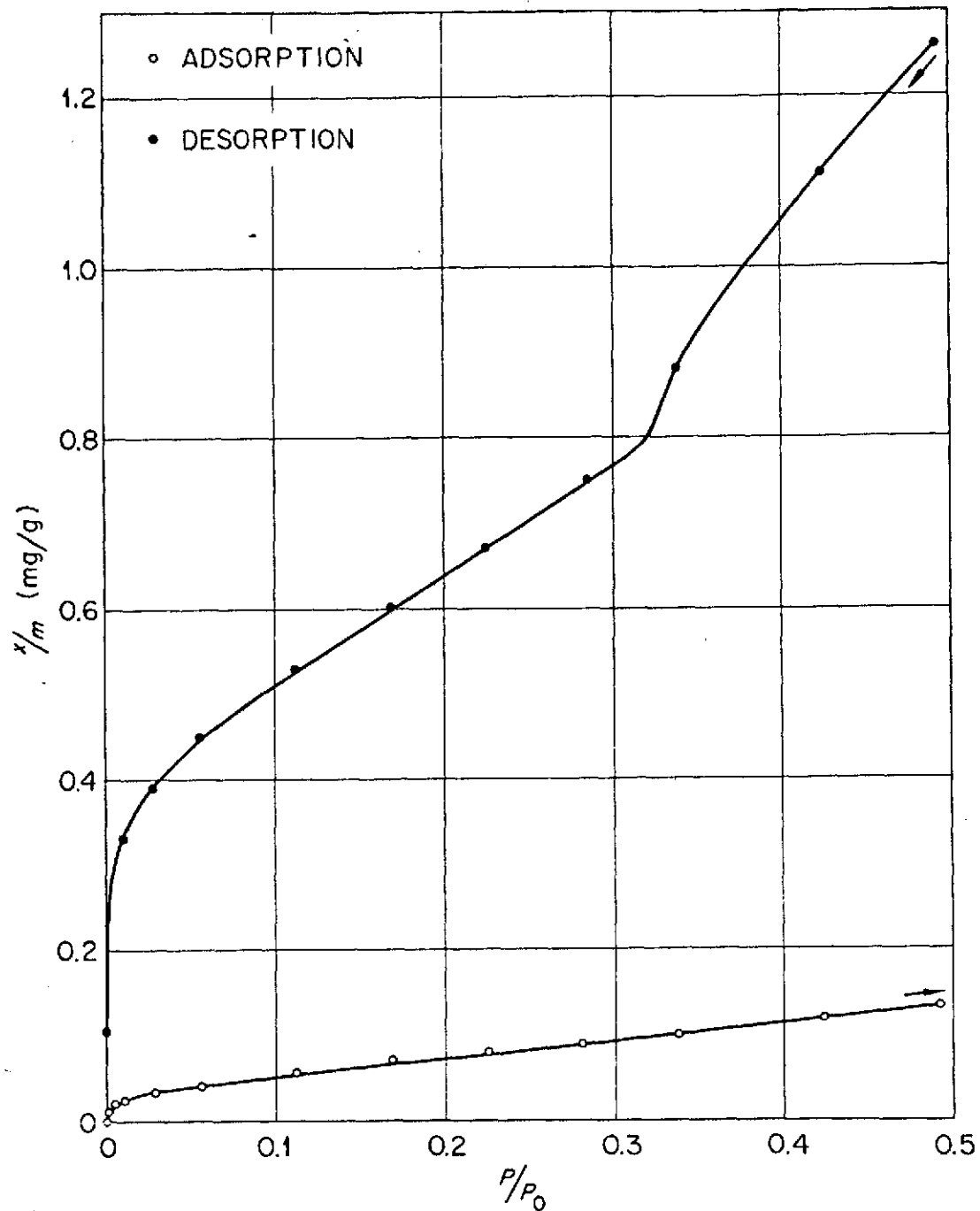
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Fig. 3. Adsorption of H_2O on 74220,35 at 20 °C
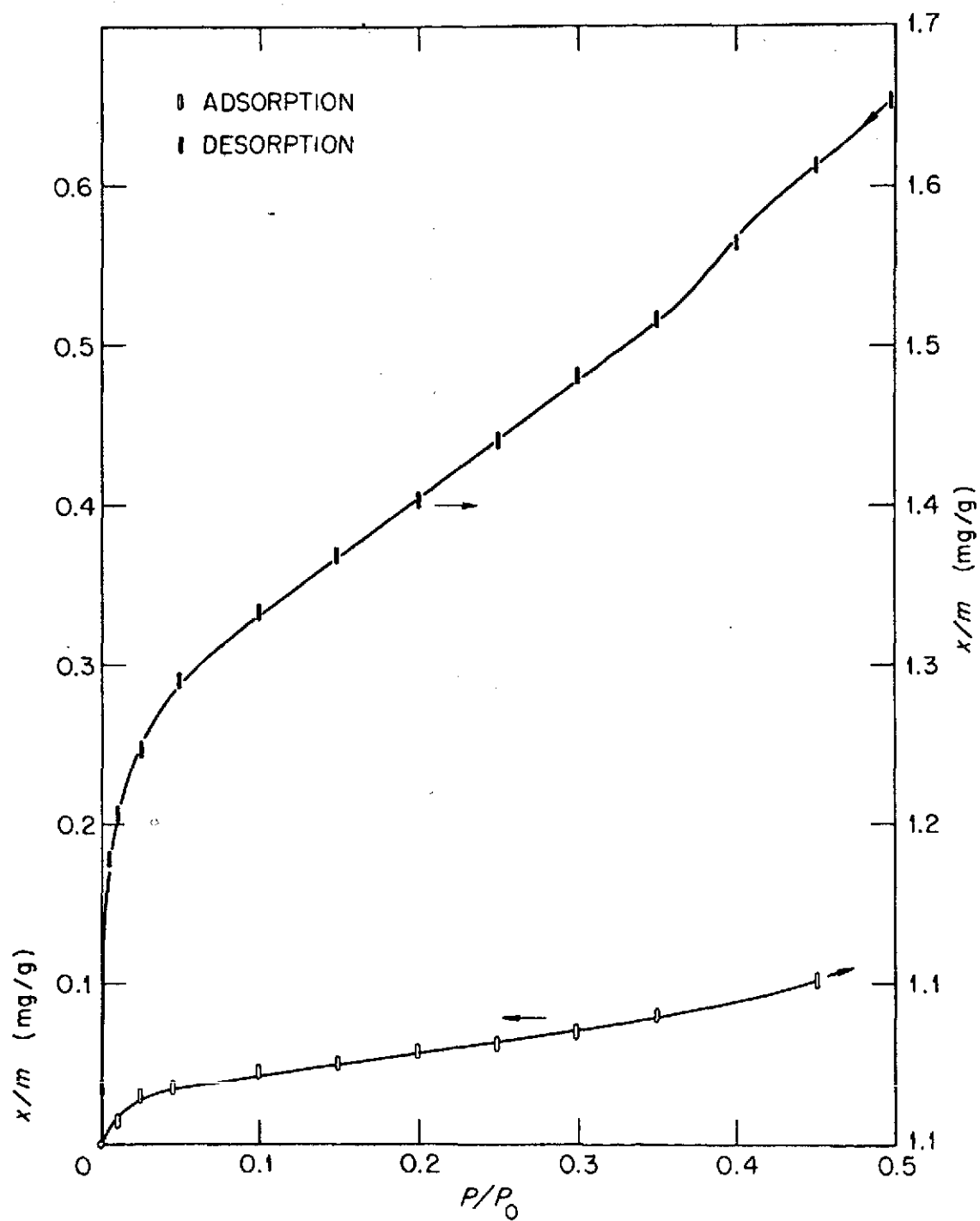Sample Outgassed at 300 °C.

Fig. 4. Adsorption of H_2O on 74241,42 at 22°C. Sample Outgassed at 300°C.
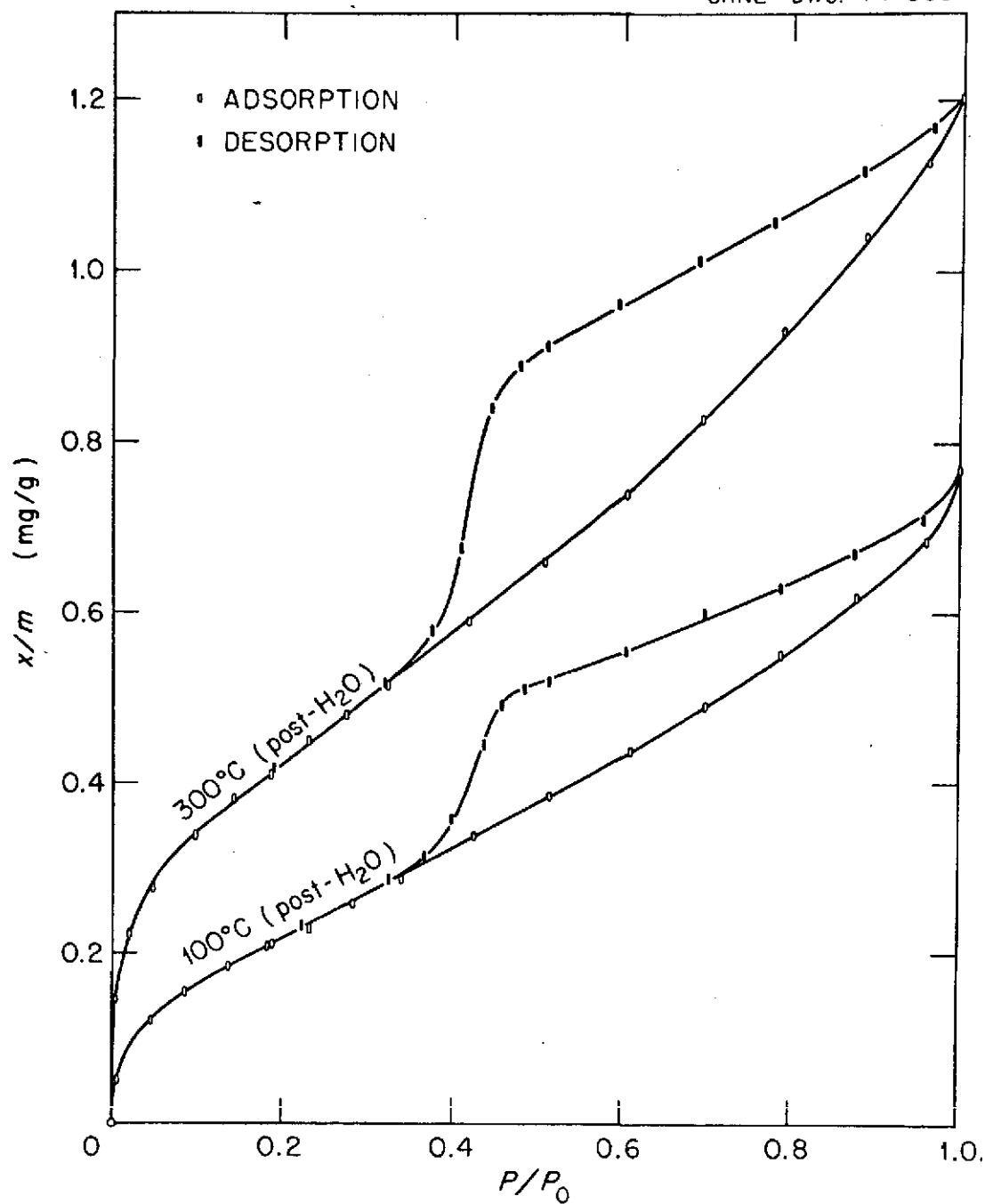
ORNL-DWG. 74-809

Fig. 5. Adsorption of O_2 on 74220,35 at 77°K.
Sample Outgassed at Indicated Temperature.